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Reverse-Saturable Absorption in Aluminophthalocyanine-Doped Xerogels

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Abstract. Aluminophthalocyanines were encaged in different silica xerogel matrices. Nonlinear reverse-saturable absorption behavior was observed for both nanosecond and picosecond pulse excitation at 532 nm. In order to determine the relaxation paths of the molecules after optical excitation, we measured the evolution of the transmission of a continuous probe beam through the samples following absorption induced by a pump pulse. The transmission recovery was a few tens of microseconds. The fluorescence lifetime was about 10 ns.

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Some solutions of organic molecules present, at given wavelengths, reverse saturable absorption behavior: they are transparent for low-energy pulses and absorbent for high-energy pulses. The reason for this behavior is that the excited states are more absorbent than the ground states at certain wavelengths and that these first excited states have long lifetimes (Fig. 1). Such materials should be of great interest for applications like mode locking or optical limiting and they have already been extensively studied in solution [1–4]. Using the sol-gel process, which allows the incorporation of organic molecules in solid vitreous matrices at low temperatures, it is now possible to encage some of these molecules in solid xerogel matrices [5, 6]. We have studied reverse saturable absorption of such samples doped with aluminophthalocyanines and excited at 532 nm. The results presented in this communication are all related to single-shot experiments.

Aluminophthalocyanine doped oxide gel matrices were synthesized by hydrolysis-condensation of silicon alkoxides. Three silicon precursors have been used: the well-known TetraEthOxySilane (TEOS) and two alkylsilanes ($CH_2=CH\text{-}Si(OEt)_3$ and $CH_3\text{-}Si(OEt)_3$ having Vinyl (VTEOS) and Methyl (MTEOS) groups as residual organic part. Hydrolysis was performed under acid-catalyzed conditions with ethanol as the common solvent. The molar ratios of alkoxide: water: ethanol were 1:3:3, respectively. After complete hydrolysis of the alkoxy groups, solutions were concentrated under reduced pressure. Aluminophthalocyanine dissolved in ethanol was added to the resulting sols. Dye concentrations were 4×10^{-4} mol/l. The mixtures were poured into poly-propylene cylindrical-shaped moulds, covered with aluminum foil and maintained at 40° C until the gels were completely dry and solid. Gelation and aging times were one week and one month, respectively. Optically clear xerogels of approximately 70 mm diameter and 1 mm thickness were obtained. These samples did not require polishing prior to optical measurements.

The Reverse-Saturable Absorber (RSA) behavior in a nanosecond regime was studied with the following experimental setup (Fig. 2). The samples were irradiated with 8 ns optical pulses, linearly polarized at a wavelength of 532 nm. The pulses were obtained from a frequency-doubled Nd:YAG laser. The laser beam was

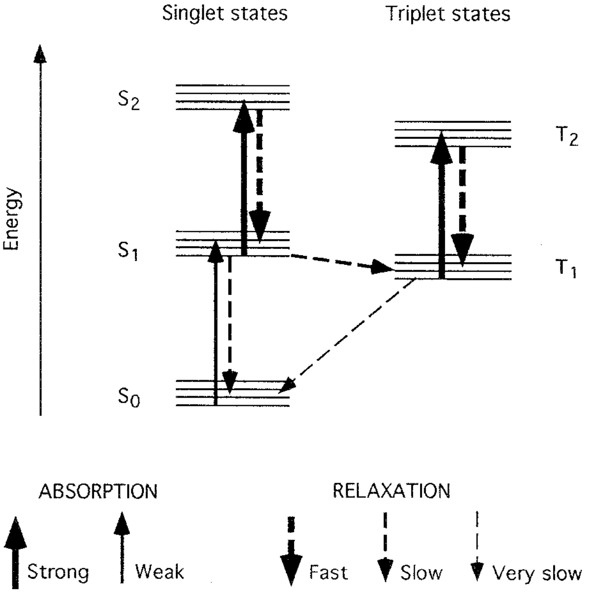

Fig. 1. Schematic five-energy-level model of organic molecules, considering singlet and triplet states

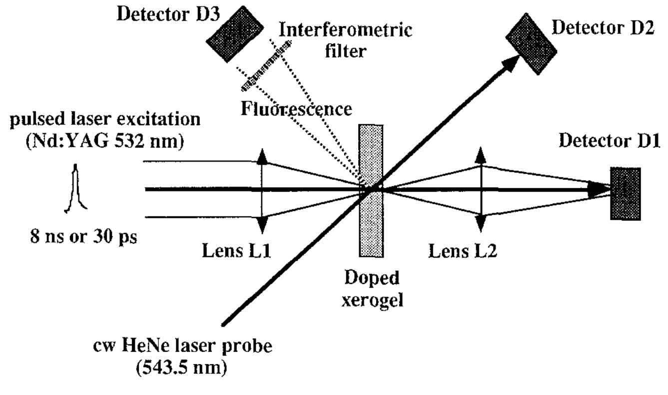

Fig. 2. Experimental setup used to measure the following data: transmission of the samples for nanosecond pulses or picosecond pulses from frequency-doubled Nd:YAG lasers, transmission recovery of a cw-HeNe laser after the excitation by a pump pulse from a nanosecond Nd:YAG laser through the different samples and the fluorescence lifetime of the samples after optical excitation by a picosecond Nd:YAG laser

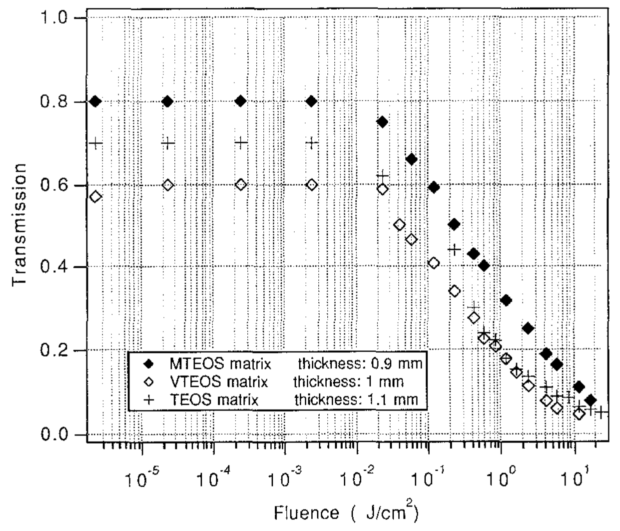

Fig. 3. Measurements of the transmission of three different matrices doped with aluminophthalocyanines as a function of incident fluence of optical pulses from a nanosecond frequency-doubled Nd:YAG laser

focused on the sample to a surface of about 200 μm of diameter. With the detector D1, we measured the transmission of each sample for different incident energies from 1 nJ (3 μJ/cm^2) to 10 mJ (30 J/cm^2). The experimental results are reported in Fig. 3 for the three different samples. With the TEOS matrix, the nonlinear effect appeared for energies of a few μJ, which corresponds to a fluence of about 10 mJ/cm^2. We observed a difference of transmission from the linear value of 70% ($D=0.15$) to 7% ($D=1.15$), wich corresponds to an induced optical density of $D=1$. The experimental points corresponding to incident energies higher than 3 mJ (10 J/cm^2, thus 1.3 GW/cm^2) must be considered with caution because they correspond to the damage threshold of the matrix. As shows in Fig. 3, similar results are obtained with the MTEOS and VTEOS matrices.

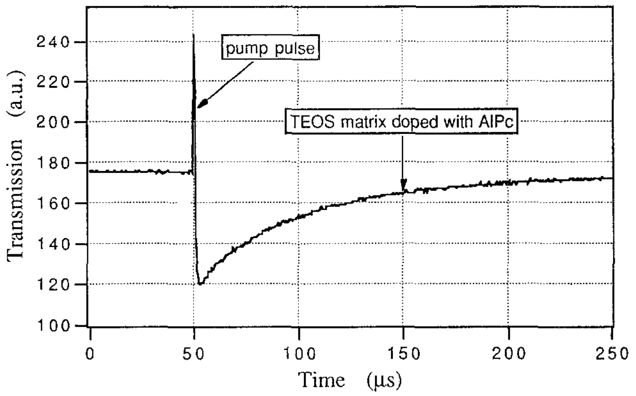

Fig. 4. Measurement of the variation of the transmission of a cw-HeNe laser at 543.5 nm after a pump pulse from a nanosecond frequency-doubled Nd:YAG laser through a TEOS matrix doped with aluminophthalocyanines

To measure the recovery time of the induced absorption, we used a continuous-wave (cw) probe beam (Fig. 2). The samples were again irradiated by the nanosecond Nd:YAG laser at 532 nm, but we focused a cw-HeNe beam at 543.5 nm on the irradiated area. A fast photodiode D2 detected the variation of the transmitted intensity of the cw-laser beam. Without the Nd:YAG pulse, the linear transmission of the TEOS sample was 70% as for the low-energy Nd:YAG pulses. As the sample was illuminated by the pump pulse, its transmission decreased and then recovered to its initial value. We recorded this recovery time: an experimental curve, shown in Fig. 4, represents the transmission of the cw-laser beam through a TEOS matrix doped with Alumino-Phthalocyanine (AlPc) before, during and after a single pump pulse. The recovery time of the transmission was then fit with a monoexponential function giving a lifetime constant of about 60 μs. For all samples, we observed a decrease in the transmission after the excitation (the initial increase of the transmission observed in Fig. 4 corresponds to the scattering of the pump pulse). The different recovery times were about 35 μs for the MTEOS matrix and 16 μs for the VTEOS matrix. The relaxation times of triplet states are known to be longer than singlet-state lifetimes [3,4,7]. Thus, the order of magnitude of the recovery time we measured tend to indicate that the excited molecules were, most of the time, in triplet states where the absorption was still significant at this wavelength (Fig. 1). This experiment shows the influence of the triplet states on the "RSA" phenomenon, it was therefore interesting to see if the samples exhibit the same reverse-saturable absorption behavior when the triplet states did not operate. As the decay time from singlet to triplet states is estimated to be a few nanoseconds [3,4,7], we studied the RSA behavior with picosecond pulses. In a few picoseconds, the AlPc molecules excited by the optical pulse should not have time to relax to triplet states.

Thus, to observe singlet-state properties, we modified the experimental setup (Fig. 2) replacing the nanosecond Nd:YAG laser with a picosecond Nd:YAG laser. The samples were irradiated by 30 ps pulses at a wavelength

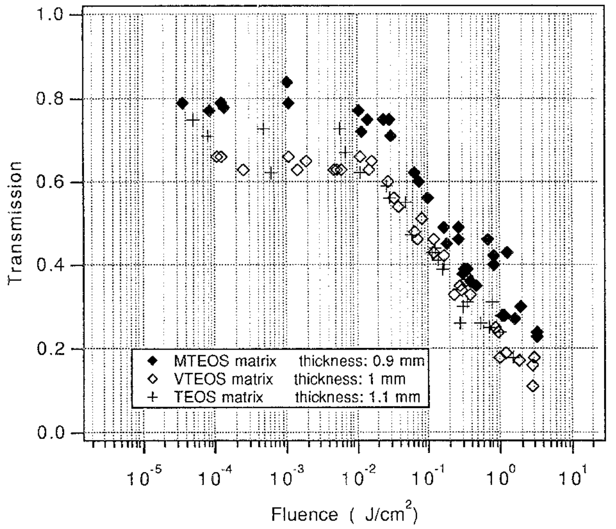

Fig. 5. Measurements of the transmission of three different matrices doped with aluminophthalocyanines as a function of incident fluence of optical pulses from a picosecond frequency-doubled Nd:YAG laser

$\lambda = 532$ nm. As the picosecond-laser energy output was very unstable, it was necessary to add a reference in order to compare the transmitted energy and the incident energy for each pulse. The laser beam was focused on the sample to an irradiated surface of about 70 μm diameter. With detector D1 we measured the transmission of the samples for intensities varying from 1 nJ to 200 μJ (25 μJ/cm^2 to 5 J/cm^2). The experimental results, reported in Fig. 5, represent the variation of the transmission of the sample as a function of the incident fluence. Our results showed that the samples present RSA behavior with picosecond-pulses. For the TEOS matrix, the threshold for nonlinear effects was 0.6 μJ/pulse (about 15 mJ/cm^2). We observed a change in transmission from 70% ($D = 0.15$) to 22% ($D = 0.65$), which corresponds to an induced optical density $D = 0.5$. The matrix damage threshold was about 30 μJ/pulse (about 0.8 J/cm^2 thus 26 GW/cm^2) under these conditions. Figures 3 and 5 show a similar order of magnitude for transmission of the sample as a function of energy fluence, but the energy damage threshold is lower in the picosecond case. This shows that not many molecules have time to reach the first excited triplet state during the 8 ns pulse and/or that the absorption cross section of the first excited singlet and triplet states are similar.

Using this picosecond laser as a brief excitation, we also measured the fluorescence lifetime of the sample with a fast photodiode D3, which detected the fluorescence signal around 700 nm due to the $S_1 \rightarrow S_0$ relaxation (Fig. 2). Interferometric filters were used to eliminate the 532 nm signal coming from the scattering of the pump by the sample. The overall time response of our system was 1 ns. A monoexponential fit function of the fluorescence signal gave us the expected lifetime. It gave us data concerning the decay time of the electrons from the first excited singlet state S_1 of the aluminophthalocyanine molecules (Fig. 1). All the different samples were tested. We observed no difference between the samples of AlPc in the two mixed organic/inorganic matrices MTEOS and VTEOS, and we obtained a time of about $\tau \approx 13$ ns. For the inorganic TEOS matrix, this time was shorter namely 9.5 ns.

These results show the reverse-saturable absorption behavior of aluminophthalocyanine doped xerogels at 532 nm and suggest their possible use for optical limiting. The experimental results were similar in the nanosecond and picosecond regimes. Small differences were seen between the different host matrices, especially between the inorganic and the mixed organic/inorganic matrices, the former having stronger interactions with the dopant molecules. The ultrafast induced optical densities were equal to 1 for our best sample with nanosecond pulses and were about 0.5 with the same sample using picosecond pulses. Experiments using a cw laser to measure the kinetics of the transmission recovery of a sample after a pump pulse of a few tens of μs, indicates that some of the excited molecules relax through the first excited triplet state whose lifetime is relatively long. Thus, we now dispose of sufficient data to model the reverse saturable absorption phenomenon in our sample using a five-energy-level model that includes the triplet states. Concurrently, other phthalocyanine doped xerogels are being studied in order to investigate the influence of the matrices on the optical properties of the dopants.

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